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(54) **SCREEN COATING COMPOSITION AND METHOD FOR APPLYING SAME**

**BILDSCHIRMBESCHICHTUNGSZUSAMMENSETZUNG UND VERFAHREN ZU DEREN
ANWENDUNG**

COMPOSITION POUR SERIGRAPHIE ET METHODE D'APPLICATION

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(56) References cited:
US-A- 4 374 222 US-A- 5 242 958
US-A- 5 426 138 US-A- 5 889 076
US-A- 5 916 669

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a water-free, water-washable, energy-curable, polymer-forming composition, especially useful as a print screen coating, and a method for applying same.

2. Background of the Art

[0002] In silk screen printing, the ink is forced onto a printing substrate through a stencil, or "mask", having a porous screen area configured in the shape of the indicia to be printed, such as letters or graphic images. The printing substrate can be paper, textile, metal, ceramic, polymer film, and the like. The screen can be a gauze or mesh fabricated from metal, textile fabric such as silk or cotton, or various polymer materials.

[0003] The mask is generally prepared by coating a screen with a curable composition, curing the composition, and then engraving the indicia. The engraved areas are porous, thereby permitting ink to be forced through the screen onto the printing substrate to print the indicia.

[0004] After printing, the ink on the substrate is cured or hardened by any of several methods such as, for example, exposure of the ink to energy such as heat or radiation (e.g. ultraviolet, electron beam, and the like), evaporation of a solvent in the ink composition, or oxidation hardening of drying oil components (e.g. linseed oil, tung oil), and the like.

[0005] The three main technologies being practiced today which make up the bulk of the coatings and inks include solvent borne, water borne, and zero volatile organic compounds (VOC). Solvent borne and water borne systems produce coatings which are washable. Water washability is a desired feature of a coating composition since the coating application equipment needs to be cleaned for reuse. However, there has been a technological push to eliminate organic solvents and water in such compositions. Organic solvents present environmental health concerns. And both solvent based and water based systems are energy intensive, requiring drying ovens to remove the solvent or water. For example, thermally induced drying and curing of coated screen fabric typically requires about 7,000 to 12,000 kilojoules of energy per kilogram of fabric as well as a long curing time, typically several hours. Consequently, what is desired is a waterless, yet water-dispersible, zero VOC composition which would be particularly useful as a coating for a print screen.

[0006] US-A-4,374,222 discloses a mold-release composition comprising a mixture of at least one relatively high equivalent weight hydroxyl-containing materials having an average active hydrogen functionality of from 2 to 8, preferably from 2 to 4 and an average active

hydrogen equivalent weight of from 500 to 5000, preferably from 1000 to 3000 and at least one relatively low equivalent weight active hydrogencontaining material including one or more of any such materials containing either hydroxyl groups, primary amine groups, secondary amine groups or mixtures of such groups; such materials having an average active hydrogen functionality of from 2 to 16, preferably from 2 to 8 and an average active hydrogen equivalent weight of from 15 to 500, preferably from 32 to 200 and when the active hydrogen atoms are derived only from OH groups then the maximum equivalent weight is 200, and an effective quantity of at least one fatty acid amide having at least one of the hydrogen atoms attached to the nitrogen atom of an amide group replaced with a-hydroxyl-containing substituent.

SUMMARY OF THE INVENTION

[0007] In accordance with the present invention, a substantially water-free, water-washable, energy-curable, polymer-forming composition is provided which comprises:

- a) an oligomer selected from the group consisting of epoxy oligomer and urethane oligomer, said oligomer having at least two polymerizable ethylenically unsaturated moieties;
- b) at least one alkoxyolated polyol monomer having at least two polymerizable ethylenically unsaturated moieties and capable of being copolymerized with oligomer component (a) to provide a solid cured polymer when exposed to energy-polymerizing conditions; and,
- c) at least one surface active agent capable of being integrated into the molecular structure of the polymer resulting from the copolymerization of (a) and (b) either by covalent bonding or by hydrogen bonding, and further capable of rendering said composition water-dispersible.

[0008] Also provided herein is a method for coating a screen with the aforementioned composition employing applicator means which can be washed with water.

[0009] The foregoing composition contains substantially no VOCs and is readily dispersible in water. Another advantage of this composition is that it significantly reduces the amount of energy and time required to effect curing.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] While the present invention is particularly applicable to coatings for print screens, it should be understood that any coating application or substrate, for printing or non-printing purposes, is within its scope. Percentages of materials are by weight unless stated oth-

erwise.

[0011] The substantially water-free, water-washable, energy-curable, poly-forming composition herein includes an epoxy oligomer and/or urethane oligomer having at least two polymerizable ethylenically unsaturated moieties, an alkoxyated polyol monomer having at least two ethylenically unsaturated moieties and a surface active agent which is copolymerizable with the oligomer and/or monomer.

[0012] An aliphatic and/or aromatic urethane oligomer may optionally be employed instead of, or in addition to, the epoxy oligomer. The urethane oligomer component is preferably a urethane acrylate such as, for example, PHOTOMER® 6008 available from Henkel Corporation. However, the epoxy oligomer is preferred.

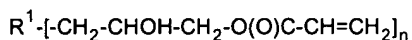
[0013] Also, the epoxy oligomer may optionally be accompanied by polyester acrylate oligomer, trimethylol propane dimerester tetraacrylate oligomer, or dipolyoxypropylene glycerol adipate oligomer.

[0014] Generally, the energy-curable composition of the present invention includes the following component weight percentages:

Oligomers	30% - 70%
Monomers	30% - 70%
Surfactants	0.1% to 20%
Photoinitiators	0 - 10%

[0015] The epoxy oligomer can be prepared by reacting an epoxide with an unsaturated acid such as acrylic or methacrylic acid, optionally in the presence of a polyamide derived from a polymerized fatty acid.

[0016] In one embodiment the epoxy acrylate oligomer is derived from a compound having the formula:



wherein R^1 is an aliphatic, aromatic or arene moiety having at least two carbon atoms and at least two oxido residues, and n is an integer of from 2 to 6.

[0017] Useful epoxides include the glycidyl ethers of both polyhydric phenols and polyhydric alcohols, epoxidized fatty acids or drying oil acids, epoxidized diolefins, epoxidized di-unsaturated acid esters, as well as epoxidized unsaturated polyesters, preferably containing an average of more than one epoxide group per molecule. The preferred epoxy compounds will have a molecular weight of from 300 to 600 and an epoxy equivalent weight of between 150 and 1,200.

[0018] Representative examples of the epoxides include condensation products of polyphenols and (methyl)epichlorohydrin. For the polyphenols, there may be listed bisphenol A, 2,2'-bis(4-hydroxyphenyl)methane (bisphenol F), halogenated bisphenol A, resorcinol, hydroquinone, catechol, tetrahydroxyphenylethane, phenol novolac, cresol novolac, bisphenol A novolac and

bisphenol F novolac. There may also be listed epoxy compounds of the alcohol ether type obtainable from polyols such as alkylene glycols and polyalkylene glycols, e.g. ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, glycerine, diglycerol, trimethylolpropane, pentaerythritol, inositol, sorbitol, polyethylene glycol, polypropylene glycol, polytetrahydrofuran, (i.e., poly(1,4-butanediol)), which is obtainable under the designation TERATHONE® from DuPont), and alkylene oxide-adduct of bisphenols, and (methyl)epichlorohydrin; glycidyl amines obtainable from anilines such as diaminodiphenylmethane, diaminophenylsulfone and p-aminophenol, and (methyl)epichlorohydrin; glycidyl esters based on acid anhydrides such as phthalic anhydride and tetrahydro- or hexahydro- phthalic anhydride; and alicyclic epoxides such as 3,4-epoxy-6-methylcyclohexylmethyl and 3,4-epoxy-6-methylcyclohexyl carboxylate.

[0019] Glycidyl polyethers of polyhydric phenols are made from the reaction of a polyhydric phenol with epihalohydrin or glycerol dihalohydrin, and a sufficient amount of caustic alkali to combine with the halogen of the halohydrin. Glycidyl ethers of polyhydric alcohols are made by reacting at least about 2 moles of an epihalohydrin with 1 mole of a polyhydric alcohol such as ethylene glycol, pentaerythritol, etc., followed by dehydrohalogenation.

[0020] In addition to polyepoxides made from alcohols or phenols and an epihalohydrin, polyepoxides made by the known peracid methods are also suitable. Epoxides of unsaturated esters, polyesters, diolefins and the like can be prepared by reacting the unsaturated compound with a peracid. Preparation of polyepoxides by the peracid method is described in various periodicals and patents and such compounds as butadiene, ethyl linoleate, as well as di- or tri-unsaturated drying oils or drying oil acids, esters and polyesters can all be converted to polyepoxides. Epoxidized drying oils are also well known, these polyepoxides usually being prepared by reaction of a peracid such as peracetic acid or performic acid with the unsaturated drying oil according to U. S. -A- 2,569,502.

[0021] In certain embodiments, the diepoxide is an epoxidized triglycerides containing unsaturated fatty acids. The epoxidized triglyceride may be produced by epoxidation of one or more triglycerides of vegetable or animal origin. The only requirement is that a substantial percentage of diepoxide compounds should be present. The starting materials may also contain saturated components. However, epoxides of fatty acid glycerol esters having an iodine value of 50 to 150 and preferably 85 to 115 are normally used. For example, epoxidized triglycerides containing 2% to 10% by weight of epoxide oxygen are suitable. This epoxide oxygen content can be established by using triglycerides with a relatively low iodine value as the starting material and thoroughly epoxidizing them or by using triglycerides with a high

iodine value as starting material and only partly reacting them to epoxides. Products such as these can be produced from the following fats and oils (listed according to the ranking of their starting iodine value): beef tallow, palm oil, lard, castor oil, peanut oil, rapeseed oil and, preferably, cottonseed oil, soybean oil, train oil, sunflower oil, linseed oil. Examples of typical epoxidized oils are epoxidized soybean oil with an epoxide value of 5.8 to 6.5, epoxidized sunflower oil with an epoxide value of 5.6 to 6.6, epoxidized linseed oil with an epoxide value of 8.2 to 8.6 and epoxidized train oil with an epoxide value of 6.3 to 6.7.

[0022] Further examples of polyepoxides include the diglycidyl ether of diethylene glycol or dipropylene glycol, the diglycidyl ether of polypropylene glycols having molecular weight up to, for example, 2,000, the triglycidyl ether of glycerine, the diglycidyl ether of resorcinol, the diglycidyl ether of 4,4'-isopropylidene diphenol, epoxy novolacs, such as the condensation product of 4,4'-methylenediphenol and epichlorohydrin and the condensation of 4,4'-isopropylidenediphenol and epichlorohydrin, glycidyl ethers of cashew nut oil, epoxidized soybean oil, epoxidized unsaturated polyesters, vinyl cyclohexene dioxide, dicyclopentadiene dioxide, dipentene dioxide, epoxidized polybutadiene and epoxidized aldehyde condensates such as 3,4-epoxycyclohexyl methyl-3',4'-epoxycyclohexane carboxylate.

[0023] Particularly preferred epoxides are the glycidyl ethers of bisphenols, a class of compounds which are constituted by a pair of phenolic groups interlinked through an intervening aliphatic bridge. While any of the bisphenols may be used, the compound 2,2-bis (p-hydroxyphenyl) propane, commonly known as bisphenol A, is more widely available in commerce and is preferred. While polyglycidyl ethers can be used, diglycidyl ethers are preferred. Especially preferred are the liquid Bisphenol A-epichlorohydrin condensates with a molecular weight in the range of from 300 to 600.

[0024] The acid component is comprised of an ethylenically unsaturated acid. Particularly suitable ethylenically unsaturated monocarboxylic acid are the alpha, beta-unsaturated monobasic acids. Examples of such monocarboxylic acid monomers include acrylic acid, beta-acryloxypropionic acid, methacrylic acid, crotonic acid, and alpha-chloroacrylic acid. Preferred examples are acrylic acid and methacrylic acid. Also suitable acid components are adducts of hydroxyalkyl acrylates or hydroxyalkyl methacrylates and the anhydrides of dicarboxylic acids such as, for example, phthalic anhydride, succinic anhydride, maleic anhydride, glutaric anhydride, octenylsuccinic anhydride, dodecenylsuccinic anhydride, chlorendic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride and methyltetrahydrophthalic anhydride. Such adducts can be prepared by methods of preparative organic chemistry known in the art. The acid component can also contain other carboxylic acids. In certain embodiments, the acid component will be comprised of a minor amount, e.g. less than

50% of the total acid equivalents, more typically less than 20% of the total acid equivalents, of a fatty acid. The fatty acids are saturated and/or unsaturated aliphatic monocarboxylic acids containing 8 to 24 carbon atoms or saturated or unsaturated hydroxycarboxylic acids containing 8 to 24 carbon atoms. The carboxylic acids and/or hydroxycarboxylic acids may be of natural and/or synthetic origin. Examples of suitable monocarboxylic acids are caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, myristic acid, palmitic acid, palargonic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linoleic acid, linolenic acid, elaeostearic acid, conjugated fatty acid, ricinoleic acid, arachic acid, gadoleic acid, behenic acid, erucic acid and brassidic acid and the technical mixtures thereof obtained, for example, in the pressure hydrolysis of natural fats and oils, in the oxidation of aldehydes from Roelen's oxo synthesis, or as monomer fraction in the dimerization of unsaturated fatty acids. In a particularly preferred embodiment, the fatty acid is derived from technical mixtures of the fatty acids mentioned which are obtainable in the form of the technical mixtures typically encountered in oleochemistry after the pressure hydrolysis of oils and fats of animal or vegetable origin, such as coconut oil, palm kernel oil, sunflower oil, rape oil, rapeseed oil and coriander oil and beef tallow. However, the fatty acid may also contain a branched fatty acid residue, for example the residue of 2-ethyl hexanoic acid, isopalmitic acid or isostearic acid.

[0025] Preferred fatty acids are mixtures obtained from natural sources, e.g. palm oil, palm kernel oil, coconut oil, rapeseed oil (from old high-erucic acid plants or from new low-erucic acid plants, a.k.a. canola oil), sunflower oil (from old lowoleic plants or from new high-oleic plants), castor oil, soybean oil, cottonseed oil, peanut oil, olive oil, olive kernel oil, coriander oil, castor oil, meadowfoam oil, chaulmoogra oil, tea seed oil, linseed oil, beef tallow, lard, fish oil and the like. Naturally occurring fatty acids typically are present as triglycerides of mixtures of fatty acids wherein all fatty acids have an even number of carbon atoms and a major portion by weight of the acids have from 12 to 18 carbon atoms and are saturated or mono-, di-, or tri-unsaturated.

[0026] The preferred epoxy resins, i.e., those made from bisphenol A, will have two epoxy groups per molecule. Thus, the product of a reaction with acrylic or methacrylic acid will contain an epoxy (meth)acrylate compound having a main chain of polyepoxide and both terminals of a (meth)acrylate group, respectively. Accordingly, the stoichiometric amount of acrylic acid to form a diacrylate adduct would be two moles of acid for each two epoxy groups. In practice, however, it is preferred to use an amount of acid slightly in excess of the amount necessary to cover both epoxy groups. Therefore, the amount of acrylic acid reacted is typically between 2.001 moles to 2.1 moles, and more typically between 2.01 and 2.05 moles of acid per two epoxy groups.

[0027] Alternatively, the reaction of the epoxide and the acid can take place in the presence of a polyamide derived from a polymerized fatty acid. The polyamide preferably has a number average molecular weight of less than 10,000 grams/mole. Low melting polyamide resins melting within the approximate range of 90°C to 130°C may be prepared from polymeric fatty acids and aliphatic polyamines. Typical of the polyamines which may be used are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-diaminobutane, 1,3-diaminobutane, hexamethylene diamine, piperazine, isophorone diamine, 3-(N-isopropylamine)-propylamine, 3,3'-iminobispropylamine, and the like. A preferred group of these low melting polyamides are derived from polymeric fatty acids, and ethylene diamine and are solid at room temperature.

[0028] Suitable such polyamides are commercially available under the trade designation of VERSAMID® polyamide resins, e.g. VERSAMID® 335, 750 and 744, and are amber-colored resins having a number average molecular weight up to 10,000, preferably from 1,000 to 4,000 and a softening point from below room temperature to 190°C.

[0029] The preferred polyamide is VERSAMID® 335 polyamide which is commercially available from Henkel Corporation and has an amine value of 3, a number average molecular weight of 1699, as determined by gel permeation chromatography (GPC) using a polystyrene standard, and a polydispersity of 1.90.

[0030] The preparation of such VERSAMID® polyamide resins is well known and by varying the acid and/or functionality of the polyamine, a great variety of viscosities, molecular weights and levels of active amino groups spaced along the resin molecule can be obtained. Typically, the VERSAMID® polyamide resins useful herein have amine values from 0 to 25, preferably 0 to 10, more preferably 0 to 5; viscosities of from 0.1 to 3 Pa-s (1 to 30 poises) (at 160°C) and polydispersities of less than 5. The amine value and number average molecular weight of the polyamide can be determined as described in U.S. -A- 4,652,492 (Seiner et. al.).

[0031] The polyamide is incorporated into the composition in an amount not exceeding 50% by weight based on the combined weight of the epoxide and acid components and the polyamide. Preferably, an amount not exceeding 25% by weight is utilized and most preferred is an amount of from 5% to 15% by weight.

[0032] The reaction between the epoxide and acid can be performed over a wide range of temperatures, e.g. from 40°C to 150°C., more typically from 50°C to 130°C and preferably between 90°C and 110°C, at atmospheric, sub-atmospheric or superatmospheric pressure; preferably in an inert atmosphere. Esterification is continued until an acid number of 2 to 15 is obtained. This reaction ordinarily takes place in 8 to 15 hours. To prevent premature or undesirable polymerization of the product or the reactants, it is advantageous to add a vinyl inhibitor to the reaction mixture. Suitable vinyl po-

lymerization inhibitors include tert-butylcatechol, hydroquinone, 2,5-ditertiarybutylhydroquinone, hydroquinone-monoethyl ether, etc. Advantageously, the inhibitor is included in the reaction mixture at a concentration of 0.005 to 0.1 % by weight based on the total of the reagents.

[0033] The reaction between the epoxide and the acid proceeds slowly when uncatalyzed, and can be accelerated by suitable catalysts which preferably are used, such as, for example, the tertiary bases such as triethyl amine, tributylamine, pyridine, dimethylaniline, tris (dimethylaminomethyl)-phenol, triphenyl phosphine, tributyl phosphine, tributylstilbine; alcoholates such as sodium methylate, sodium butylate, sodium methoxycarbonate, etc.; quaternary compounds such as tetramethylammonium bromide, tetramethylammonium chloride, benzyl-trimethylammonium chloride, and the like. At least 0.01 percent, based on total weight of reagents, preferably at least 0.1 percent, of such catalyst is desirable.

[0034] Typical examples of suitable monomers which can be used and added to the reaction mixture before or during the reaction, or added after the reaction, as a reactive diluent, are the vinyl or vinylidene monomers containing ethylenic unsaturation, and which can copolymerized with the compositions of this invention are, styrene, vinyl toluene, tertiary butyl styrene; alpha-methylstyrene, monochlorostyrene, dichlorostyrene, divinylbenzene, ethyl vinyl benzene, diisopropenyl benzene, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylonitrile, methacrylonitrile, the vinyl esters, such as vinyl acetate and the monovinyl esters of saturated and unsaturated aliphatic, monobasic and polybasic acids, such as the vinyl esters of the following acids: propionic, isobutyric, caproic, oleic, stearic, acrylic, methacrylic, crotonic, succinic, maleic, fumaric, itaconic hexahydrobenzoic, citric, tartaric, etc., as well as the corresponding allyl, methallyl, etc., esters of the aforementioned acids, the itaconic acid monoesters and diesters, such as the methyl, ethyl, butyl esters, etc.; the maleic and fumaric acid monoesters, diesters and their amide and nitrile compounds, such as diethyl maleate, maleyl tetramethyl diamide, fumaryl dinitrile, dimethyl fumarate; cyanuric acid derivatives having at least one copolymerizable unsaturated group attached directly or indirectly to the triazine ring such as diallyl ethyl cyanurate, triallyl cyanurate, etc., ethers such as vinyl allyl ether, divinyl ether, diallyl ether, resorcinol divinyl ether, etc., diallyl chlorendate, diallyl tetrachloro phthalate, diallyl tetrabromophthalate, dibromopropargyl acrylate, as well as the partial fusible or soluble polymerizable polymers of the hereinabove listed monomers, etc.

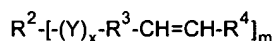
[0035] In preparing the polymerizable compositions containing the reaction product of this invention and one or more of the monomers of the type listed hereinabove, the relative amount of the monomers can vary broadly. In general, however, the monomer or monomers are

used at less than 50% by weight of the composition, typically in the range of 1% to 30% by weight, and more typically in the range of 5% to 15% by weight.

[0036] Epoxy oligomers prepared by reacting an epoxide with acrylic acid in the presence of a polyamide derived from a polymerized fatty acid possess the advantage of being thixotropic. The viscosity of compositions containing such oligomers decreases with the application of increasing agitation or shear stress and gradually returns to its former viscous state when allowed to rest. Thus, the composition exhibits lower viscosity when in the process of being applied to a substrate under the application of force or pressure. However, once the coating has been applied it resumes its high viscosity state and tends to remain on the substrate without running.

[0037] Also, epoxy oligomer may optionally be accompanied by polyester acrylate oligomer, trimethylol propane dimerester tetraacrylate oligomer, or dipolyoxypropylene glycerol adipate oligomer.

[0038] Referring now to the alkoxyated polyol component of the composition described herein, the preferred alkoxyated polyol monomer has the formula.



wherein R^2 is an aliphatic, aromatic or arene moiety having at least two carbon atoms and at least two oxido residues, Y is an alkylene oxide moiety and x is an integer of from 2 to 6, R^3 is a linkage group capable of joining the alkylene oxide moiety Y and the $-CH=CH-$ group, R^4 is hydrogen or $-C(O)OR^5$ wherein R^5 is hydrogen or an alkyl group of from 1 to 22 carbon atoms, and m is an integer of from 2 to 6.

[0039] More particularly, R^2 can be an ethylene glycol residue, propylene glycol residue, trimethylol propane residue, pentaerythritol residue, neopentyl glycol residue, glyceryl residue, diglyceryl residue, inositol residue, sorbitol residue, hydroquinone residue, catechol residue, or bisphenol residue (e.g. bisphenol A). R^2 can also be selected from saturated or unsaturated straight or branched chain aliphatic moieties of from 6 to 24 carbon atoms such as epoxidized soy bean oil residue. Alternatively, R^2 can be polyethylene glycol, or ethylene oxide/propylene oxide copolymer.

[0040] Y is preferably an ethylene oxide or propylene oxide residue.

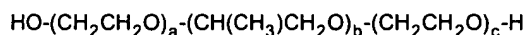
[0041] R^3 can optionally be, for example, the linking groups $-O-$, $-O(O)C-$, $-OCH_2CH_2-$, or $-OCH_2CHOHCH_2O(O)C-$.

[0042] The alkoxyated polyol monomer component preferably comprises a mixture of at least one alkoxyated polyol diacrylate such as, for example, bisphenol A ethoxylate diacrylate and/or neopentyl glycol propoxylate diacrylate, and at least one alkoxyated polyol triacrylate such as, for example trimethylolpropane ethoxylate triacrylate.

[0043] A preferred composition includes 10% to 15% by weight of neopentyl glycol propoxylate diacrylate, 5% to 10% bisphenol A ethoxylate diacrylate, and 15% to 20% trimethylolpropane ethoxylate triacrylate based on total composition weight. Preferably, also, the epoxy oligomer component used in conjunction with the alkoxyated polyol monomer component is obtained by reacting a diepoxide such as a diglycidyl ether of a dihydric phenol (e.g. bisphenol A) with an unsaturated acid component (e.g. acrylic acid) in the presence of a polyamide derived from a fatty acid.

[0044] Referring now to the surface active agent component, photopolymerizable print screen coating pastes are water insoluble, hence the need for a surface active agent capable of providing water-dispersibility so that the uncured coating paste can be washed off the application equipment. It is most efficient to include the surface active agent as part of the screen printing ink composition rather than as a component in the wash water. The surface active agents described herein are capable of being integrated into the molecular structure of the cured polymer resulting from the copolymerizable of the oligomer and the alkoxyated polyol monomer components. Integration of the surface active agent into the molecular structure of the cured polymer can be accomplished by, e.g., covalent bonding. For example, the surface active agent can include one or more active sites capable of establishing covalent bonds, such as, for example, unsaturated sites or reactive groups. Alternatively, the surface active agent can be integrated into the molecular structure of the cured polymer by means of hydrogen bonds. In either case the surface active agent possesses the advantage of not migrating within the cured coating. Moreover, integration of the surface active agent prevents water sensitivity of the cured polymer coating which would be caused by the presence of free surfactant.

[0045] One type of surface active agent found to be suitable for use in the composition of the present invention includes ethylene oxide/propylene oxide block copolymers. Such copolymers are available from BASF Corporation under the designations PLURONIC™ P105, PLURONIC™ F108, PLURONIC™ F104, and PLURONIC™ L44, for example, and have the following formula:



wherein b is at least 15 and $(CH_2CH_2O)_{a+c}$ is varied from 20% - 90% by weight.

[0046] Another type of surface active agent suitable for use in the composition of the present invention includes ethoxylated acetylenic alcohols and diols such as those available under the designations SURFYNOL® 465 and SURFYNOL® 485(W) from Air Products Co. A preferred surface active agent includes an acetylenic glycol decene diol.

[0047] Yet another type of surface active agent suitable for use in the present invention includes fluoropolymers and prepolymers such as, for example, fluorinated alkyl esters such as 2-N(alkyl perfluorooctane sulfonamido) ethyl acrylate which is available under designation FLUORAD FC-430 from 3M Co.

[0048] Yet another type of surface active agent suitable for use in the present invention includes epoxy silicones such as SILQUEST A-187 available from OSI Specialties, Inc., of Danbury, Connecticut, which has the formula:



[0049] Yet another type of surface active agent suitable for use in the present invention is a sugar surfactant such as an alkyl polyglycoside and/or a polyhydroxy fatty acid amide. Examples of suitable polyhydroxy fatty acid amides include those corresponding to formula I:



wherein R_1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R_2 is a C_5 - C_{31} hydrocarbyl moiety, preferably straight chain C_7 - C_{19} alkyl or alkenyl, more preferably straight chain C_9 - C_{17} alkyl or alkenyl, most preferably straight chain C_{11} - C_{19} alkyl or alkenyl, or mixture thereof; and Y is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxy-
lated derivative (preferably ethoxylated or propoxylated) thereof. Y preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Y is a glyceryl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Y. It should be understood that it is by no means intended to exclude other suitable raw materials. Y preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxy-
lated

derivatives thereof. Most preferred are glyceryls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$. Compounds of the formula I are also known as glucamides. Therefore, when, for example, R_1 is methyl, R_2 dodecyl; and Y is $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$, the compound in question is referred to as dodecyl N-methylglucamide.

[0050] Methods for making polyhydroxy fatty acid amides are known in the art. In general, polyhydroxy fatty acid amides can be made by reductively aminating a reducing sugar reacting with an alkyl amine to form a corresponding N-alkyl polyhydroxyamine and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride to form the N-alkyl, polyhydroxy fatty acid amide. Processes for making polyhydroxy fatty acid amides are disclosed in U.S. -A-1,985,424; 2,965,576; 5,194,639; and 5,334,764.

[0051] Examples of suitable alkyl polyglycosides include those corresponding to the formula II:



wherein R_1 is a monovalent organic radical having from 6 to 30 carbon atoms; R_2 is divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to 12; a is a number having a value from 1 to 6. Preferred alkyl polyglycosides which can be used in the compositions according to the invention have the formula I wherein Z is a glucose residue and b is zero. Such alkyl polyglycosides are commercially available, for example, as APG®, GLUCOPON®, PLANTAREN® or AGRIMUL® surfactants from Henkel Corporation, Ambler, PA, 19002. Examples of such surfactants include but are not limited to:

1. GLUCOPON® 220 Surfactant - an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and having an average degree of polymerization of 1.5.
2. GLUCOPON® 225 Surfactant - an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and having an average degree of polymerization of 1.7.
3. GLUCOPON® 600 Surfactant - an alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and having an average degree of polymerization of 1.4.
4. GLUCOPON® 625 Surfactant - an alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and having an average degree of polymerization of 1.4.
5. APG® 325 Surfactant - an alkyl polyglycoside in which the alkyl group contains 9 to 11 carbon atoms and having an average degree of polymerization of 1.6.
6. PLANTAREN® 2000 Surfactant - an alkyl polygly-

lycoside in which the alkyl group contains 8 to 16 carbon atoms and having an average degree of polymerization of 1.4.

7. PLANTAREN® 1300 Surfactant - an alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and having an average degree of polymerization of 1.6.

8. AGRIMUL® PG 2067 Surfactant - an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and having an average degree of polymerization of 1.7.

[0052] Other examples include alkyl polyglycoside surfactant compositions which are comprised of mixtures of compounds of formula I as described in U.S.-A-5,266,690 and 5,449,763.

[0053] A particularly preferred sugar surfactant for use in the present invention is an alkyl polyglycoside corresponding to formula II wherein R_1 is a monovalent organic radical having from 8 to 16 carbon atoms, b is zero, and a is a number having a value of from 1 to 2.

[0054] Generally, the surface active agent preferably constitutes from 0.1% to 20% of the total composition, more preferably 0.5% to 10%, and most preferably from 1% to 5%.

[0055] Polymerization of the energy-polymerizable composition of the present invention may be effected by the use of, for example, electron beam (EB) radiation or ultraviolet (UV) radiation. Photoinitiators are not a required component of the composition if EB radiation is used to effect polymerization. However, if UV radiation is employed the composition should include a photoinitiator.

[0056] Any photoinitiator suitable for the purposes described herein may be employed. Examples of useful photoinitiators include one or more compounds selected from benzildimethyl ketal, 2,2-diethoxy-1,2-diphenylethanone, 1-hydroxycyclohexyl-phenyl ketone, α,α -dimethoxy- α -hydroxyacetophenone, 1-(4-isopropylphenyl)-2-hydroxy-2-methyl-propan-1-one, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-propan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, 3,6-bis(2-methyl-2-morpholino-propanonyl)-9-butyl-carbazole, 4,4'-bis(dimethylamino)benzophenone, 2-chlorothioxanthone, 4-chlorothioxanthone, 2-isopropylthioxanthone, 4-isopropylthioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 4-benzoyl-N,N-dimethyl-N-[2-(1-oxo-2-propenyl)oxy]ethylbenzenemethanaminium chloride, methyl-diethanolamine, triethanolamine, ethyl 4-(dimethylamino)benzoate, 2-n-butoxyethyl 4-(dimethylamino)benzoate and combinations thereof.

[0057] Benzophenone, which is not per se a photoinitiator, may be used in photoinitiator compositions in conjunction with a coinitiator such as thioxanthone, 2-isopropyl thioxanthone, 4-isopropylthioxanthone, 2-chlorobthioxanthone, 4-chlorothioxanthone, and amine

coinitiators such as methyl-diethanolamine and ethyl 4-(dimethylamino) benzoate.

[0058] It is preferable to have a blend of photoinitiators such that the combined absorption spectra of the individual photoinitiators matches the spectral output of the UV lamp (or other radiation emitter) used to effect the curing of the coating or ink composition. For example, mercury vapor lamps have strong emissions in the UV 240 to 280 nm (2400Å to 2800Å) range and in the UV 340 to 380 nm (3400Å to 3800Å) range. By choosing a suitable blend of photoinitiators a more efficient utilization of the spectral output of the lamp can be achieved. Such increased efficiency can translate to faster throughput during the energy-polymerization process.

[0059] Moreover, coatings employing the composition described herein can include colorants such as pigments and dyes which absorb UV light. For example, pigments generally absorb wavelengths of light below 370 nm (3700Å). To cure such a coating one needs to generate free radicals by using a photoinitiator which absorbs light above 370 nm (3700Å). A suitable photoinitiator for pigmented systems includes 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, which is commercially available under the designation Irgacure 369 from Ciba-Geigy.

[0060] To insure that the composition does not prematurely polymerize, a free radical inhibitor may optionally be added to the polymerizable composition. Examples of suitable inhibitors include hydroquinone and methyl ether thereof or butylated hydroxytoluene at a level of from 5 ppm to 2000 ppm by weight of the polymerizable components. Additives which are particularly useful in prolonging the shelf-life of the composition can also be used, e.g. UV stabilizers such as Fluorstab U.V.-II from Kromachem.

[0061] The UV radiation is preferably applied to a film of the present composition at an energy density of from 2,000 to 3,000 mJ/cm², more preferably 2,200 to 2,500 mJ/cm², in order to optimize through-curing of the film. While the film can be tack free with exposure to 20-40 mJ/cm², energy densities less than 2000 mJ/cm² produce a film with a lower degree of crosslinking (as measured by pendulum hardness testing), and energy densities greater than 3000 exhibit a deleterious effect on the cured film.

[0062] The composition described herein may be applied to a screen as a coating in a conventional manner. For example, the composition can be applied by brushes, rollers, spraying or by dipping the screen in the composition. The screen can be a mesh fabricated from, for example, silk, polyester, polypropylene, high density polyethylene, nylon, glass, and metal such as nickel, aluminum, steel, etc. The coating composition is then cured or hardened by exposure to polymerizing radiation such as UV or EB radiation to form a blank stencil.

[0063] Generally, a six second exposure time is sufficient to cure the composition into a hard, tack-free coat-

ing with an energy requirement of 460kJ per kg of screen fabric.

[0064] After the screen coating is hardened, the blank stencil can be engraved, for example by means of laser light, to create porous areas in the shape of desired indicia. The engraved screen can then be used as a mask in a screen printing process in a conventional manner. The uncured composition remaining on the application equipment is readily washable with water.

[0065] The wettability of the composition described herein on a substrate such as nickel can be measured by contact angle goniometry. The present composition exhibits a contact angle on nickel of no more than 100°, more preferably no more than 70°, and most preferably no more than 30°.

[0066] The following examples are given for the purpose of illustrating the present invention.

EXAMPLE 1

[0067] A composition was made by mixing the following components:

Oligomer component:

[0068] 40% of a composition containing an epoxy oligomer obtained by reacting a diglycidyl ether of bisphenol A with acrylic acid in the presence of VERSAMID® 335 polyamide (10%) and propoxylated glycerol triacrylate (15%).

[0069] 9% dipolyoxypropylene glycerol adipate oligomer

Monomer component:

[0070] 17% trimethylol propane ethoxylate triacrylate (available from Henkel Corp. under the designation PHOTOMER® 4149).

[0071] 12.5% neopentyl glycol propoxylate diacrylate (available from Henkel Corp. under the designation PHOTOMER® 4127).

[0072] 6% bisphenol A ethoxylate diacrylate (available from Henkel Corp. under the designation PHOTOMER® 4028).

Photoinitiator component:

[0073] 0.5% blend of 2-isopropyl thioxanthone and 4-isopropylthioxanthone (available from International Bio-Synthetics under the designation Quantacure ITX).

[0074] 2.5% 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one (available from Ciba-Geigy under the designation Irgacure 907).

Pigment component:

[0075] 0.25% Irgalite Yellow.

Surface active agent component:

[0076] 12% of ethylene oxide/propylene oxide block copolymer (available from BASF under the designation Pluronic F-105).

[0077] The above components were mixed in accordance with the following procedure:

[0078] First, the epoxy acrylate oligomer, 50% of PHOTOMER® 4028, all of PHOTOMER® 4127, and the pigment were mixed together with grinding to form a ground paste. Next, the rest of the oligomer components were added to the ground paste. The surfactant mixture was prepared by blending the surface active agent with 50% of the PHOTOMER® 4149 under mild heating (less than 35°C). The surfactant blend was then added at room temperature to the ground paste with stirring. The photoinitiator was mixed with the remaining 50% of the PHOTOMER® 4149 and then added to the ground paste with mixing.

[0079] The resulting composition was self-emulsifying, had a viscosity of 2300 mPa·s (centipoise), and exhibited thixotropic shear thinning characteristics.

[0080] The composition was applied as a 50.8 µm (2 mil) thick film to screen substrates of aluminum, nickel, and steel mesh and then cured by passing the substrates under a U.V. lamp under the following conditions:

Lamp	Hg vapor
Power	300 watts/cm
Conveyor speed	6.09 m/min (20 ft./min.)
Exposure time	6 seconds
Exposure temperature	25°C

[0081] The film was observed to be tack free after one pass. The following tests were performed on the cured film.

[0082] Wettability of the metal substrates by the composition was measured using a contact angle goniometer at room temperature. The contact angle of the UV cured epoxy acrylate based film of this Example was found to be 27.5 degrees.

[0083] The hardness of the cured film, one indicator of crosslink density, was measured in accordance with ASTM D4366-92 Pendulum damping test. The cured film exhibited a hardness of 157 counts as measured by this test.

[0084] The solvent resistance of the cured film was measured by the ASTM D5402-93 MEK double rub test. The cured film was measured at more than 200 double rubs.

[0085] Adhesion of the film was assessed by a conventional tape test and by scanning electron microscope. The film exhibited sufficient adhesion.

EXAMPLE 2

[0086] A composition was made by mixing the follow-

ing components:

Oligomer component:

[0087] 37.3% of a composition containing epoxy oligomer obtained by reacting a diglycidyl ether of bisphenol A with acrylic acid in the presence of VERSAMID® 335 polyamide (10%) and propoxylated glyceryl triacrylate (15%).

Monomer component:

[0088] 18.66% trimethylol propane ethoxylate triacrylate (PHOTOMER® 4149).

[0089] 9.33% neopentyl glycol propoxylate diacrylate (PHOTOMER® 4127).

[0090] 13.99% bisphenol-A-ethoxylate diacrylate (PHOTOMER® 4028).

Photoinitiator component:

[0091] 9.52% blend of Quantacure 369 (available from International Bio Synthetics and Darocur 4265 (available from Merck)).

Pigment component:

[0092] 1.87% Irgalite yellow.

Surface active agent component:

[0093] 9.33% Ethylene oxide/propylene oxide copolymer (Pluronic 105 available from BASF).

[0094] The composition of this Example was prepared in accordance with the mixing method of Example 1. The composition was water washable. It had a viscosity of 3500 mPa·s (centipoise) and exhibited thixotropic shear thinning characteristics.

[0095] The composition was applied to a nickel screen substrate and then cured by passing the substrate under a UV lamp under the same conditions as set forth in Example 1.

[0096] The sample was observed to be tack free after one pass. The contact angle measured by a goniometer as an indicator of wettability was 27.5.

EXAMPLE 3

[0097] A composition was made by mixing the following components:

Oligomer component:

[0098] 40% of a composition containing epoxy oligomer obtained by reacting a diglycidyl ether of bisphenol A with acrylic acid in the presence of VERSAMID® 335 polyamide (10%) and propoxylated glyceryl triacrylate (15%).

[0099] 9% dipolyoxypropylene glycerol adipate oligomer.

Monomer component:

[0100] 17% trimethylol propane ethoxylate triacrylate (PHOTOMER® 4149).

[0101] 13% neopentyl glycol propoxylate diacrylate (PHOTOMER® 4127).

[0102] 6% bisphenol-A-ethoxylate diacrylate (PHOTOMER® 4028).

Photoinitiator component:

[0103] 3% 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone available as Irgacure 369.

[0104] 1% thioxanthone

Pigment component:

[0105] 1% Phthalo Blue GS

Surface active agent component:

[0106] 10% Ethylene oxide/propylene oxide copolymer (Pluronic 108 available from BASF).

[0107] The composition of this Example was prepared in accordance with the mixing method of Example 1. The composition was water washable and exhibited thixotropic shear thinning characteristics.

EXAMPLE 4

[0108] A composition was made by mixing the following components:

Oligomer component:

[0109] 25% of a composition containing epoxy oligomer obtained by reacting a diglycidyl ether of bisphenol A with acrylic acid in the presence of VERSAMID® 335 polyamide (10%) and propoxylated glyceryl triacrylate (15%).

Monomer component:

[0110] 27.25% trimethylol propane ethoxylate triacrylate (PHOTOMER® 4149).

[0111] 8% neopentyl glycol propoxylate diacrylate (PHOTOMER® 4127).

[0112] 30% bisphenol-A-ethoxylate diacrylate (PHOTOMER® 4028).

Photoinitiator component:

[0113] 2.5% Irgacure 369

[0114] 0.94% thioxanthone

Pigment component:

[0115] 0.31% Phthalo Blue GS

Surface active agent component:

[0116] 6% Ethylene oxide/propylene oxide copolymer (Pluronic 108 available from BASF).

[0117] The composition of this Example was prepared in accordance with the mixing method of Example 1. The composition was water washable and exhibited thixotropic shear thinning characteristics.

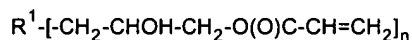
Claims

1. A substantially water-free, water-washable, energy-curable, polyiner-forming composition which comprises:

- a) an oligomer selected from the group consisting of epoxy oligomer and urethane oligomer, said oligomer having at least two ethylenically unsaturated moieties;
- b) at least one alkoxyolated polyol monomer having at least two ethylenically unsaturated moieties and capable of being copolymerized with oligomer component (a) to provide a solid cured polymer when exposed to energy-polymerizing conditions; and,
- c) a sugar surfactant selected from the group consisting of a polyhydroxy fatty acid amide, an alkyl polyglycoside, and mixtures thereof.

2. The composition of Claim 1 wherein the epoxy oligomer is an epoxy acrylate oligomer.

3. The composition of Claim 2 wherein the epoxy acrylate oligomer is derived from a compound having the formula:



wherein R¹ is an aliphatic, aromatic or arene moiety having at least two carbon atoms and at least two oxido residues, and n is an integer of from 2 to 6.

4. The composition of Claim 3 wherein R¹ is a bisphenol residue.

5. The composition of Claim 3 wherein R¹ is selected from the group consisting of hydroquinone residue and catechol residue.

6. The composition of Claim 3 wherein R¹ includes a straight or branched chain alkyl group of from 2 to 6 carbon atoms.

7. The composition of Claim 6 wherein R¹ is selected from the group consisting of ethylene glycol residue, propylene glycol residue, trimethylolpropane residue, pentaerythritol residue, neopentyl glycol residue, glyceryl residue, diglyceryl residue, inositol residue, and sorbitol residue.

8. The composition of Claim 3 wherein R¹ is a saturated or unsaturated, straight or branched chain aliphatic moiety of from 6 to 24 carbon atoms.

9. The composition of Claim 8 wherein R¹ is an epoxidized soy bean oil residue.

10. The composition of Claim 3 wherein R¹ is a polyethylene glycol moiety.

11. The composition of Claim 3 wherein R¹ is an ethylene oxide-propylene oxide copolymer.

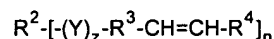
12. The composition of Claim 1 wherein the epoxy oligomer is thixotropic.

13. The composition of Claim 1 wherein the epoxy oligomer is obtained by reacting a diepoxide with an acid component having an ethylenically unsaturated carboxylic acid or reactive derivative thereof in the presence of a polyamide derived from a polymerized fatty acid.

14. The composition of Claim 13 wherein the acid component is acrylic acid.

15. The composition of Claim 13 wherein the diepoxide is a diglycidyl ether of a dihydric phenol.

16. The composition of Claim 1 wherein the alkoxyolated polyol monomer has the formula:



wherein R² is an aliphatic, aromatic, or arene moiety having at least two carbon atoms and at least two oxido residues, Y is an alkylene oxide moiety and x is an integer of from 2 to 6, R³ is a linkage group capable of joining the alkylene oxide moiety Y and the -CH=CH- group, R⁴ is hydrogen or -C(O)OR⁵ wherein R⁵ is hydrogen or an alkyl group having from 1 to 22 carbon atoms, and n is an integer of from 2 to 6.

17. The composition of Claim 16 wherein R² is a bisphenol residue or a group selected from the group consisting of hydroquinone residue and catechol residue.

18. The composition of Claim 16 wherein R² includes a

- straight or branched chain alkyl group of from 2 to 6 carbon atoms.
19. The composition of Claim 16 wherein R² is selected from the group consisting of ethylene glycol residue, propylene glycol residue, trimethylolpropane residue, pentaerythritol residue, neopentyl glycol residue, glyceryl residue, diglyceryl residue, inositol residue, and sorbitol residue.
20. The composition of Claim 16 wherein R² is a saturated or unsaturated, straight or branched chain aliphatic moiety of from 6 to 24 carbon atoms.
21. The composition of Claim 16 wherein R² is an epoxidized soy bean oil residue, a polyethylene glycol moiety or an ethylene oxide-propylene oxide copolymer.
22. The composition of Claim 16 wherein Y is an ethylene oxide residue.
23. The composition of Claim 16 wherein R³ is a member selected from the group consisting of -O-, -O(O)C-, -OCH₂CH₂- and -OCH₂CHOHCH₂O(O)C-.
24. The composition of Claim 16 wherein the at least one alkoxyated polyol monomer comprises a mixture of at least one alkoxyated polyol diacrylate and at least one alkoxyated polyol triacrylate.
25. The composition of Claim 24 wherein said composition exhibits a contact angle on nickel of no more than 100°.
26. The composition of Claim 2 4 wherein the composition includes from 5% to 30% of the at least one alkoxyated polyol diacrylate and from 5% to 30% of the at least one alkoxyated polyol triacrylate based on total composition weight.
27. The composition of Claim 2 wherein the composition includes from 10% to 25% of the at least one alkoxyated polyol diacrylate and from 10% to 25% by weight of the at least one alkoxyated polyol triacrylate based on total composition weight.
28. The composition of Claim 2 4 wherein the composition includes from 15% to 20% of the at least one alkoxyated polyol diacrylate and from 15% to 20% of the at least one alkoxyated triacrylate based on total composition weight.
29. The composition of Claim 2 4 wherein the at least one alkoxyated polyol triacrylate is trimethylolpropane ethoxylate triacrylate and the at least one alkoxyated polyol diacrylate is a member selected from the group consisting of bisphenol A ethoxylate diacrylate, neopentyl glycol propoxylate diacrylate and mixtures thereof.
30. The composition of Claim 2 9 wherein the epoxy oligomer is derived from bisphenol A epoxy diacrylate.
31. The composition of Claim 2 9 wherein the monomer mixture includes from 10% to 15% by weight of neopentyl glycol propoxylate diacrylate, and from 15% to 20% by weight of trimethylolpropane ethoxylate triacrylate, based on total composition weight.
32. The composition of Claim 31 wherein the monomer mixture further includes from 5% to 10% bisphenol A ethoxylate diacrylate.
33. The composition of Claim 31 wherein the epoxy oligomer is obtained by reacting a diepoxide with an acid component having an ethylenically unsaturated carboxylic acid or reactive derivative thereof in the presence of a polyamide derived from a polymerized fatty acid.
34. The composition of Claim 3 3 wherein the acid component is acrylic acid.
35. The composition of Claim 3 3 wherein the diepoxide is a diglycidyl ether of a dihydric phenol.
36. The composition of Claim 1 wherein the sugar surfactant is a polyhydroxy fatty acid amide corresponding to formula I:
- $$\begin{array}{c} \text{O} \quad \text{R}_1 \\ || \quad | \\ \text{R}_2 - \text{C} - \text{N} - \text{Y} \end{array} \quad (I)$$
- wherein R₁ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof; and R₂ is a C₅-C₃₁ hydrocarbyl moiety; and Y is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof.
37. The composition of Claim 1 wherein the sugar surfactant is an alkyl polyglycoside corresponding to formula II:
- $$\text{R}_1\text{O}(\text{R}_2\text{O})_b(\text{Z})_a \quad \text{II}$$

- wherein R₁ is a monovalent organic radical having from 6 to 30 carbon atoms; R₂ is divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to 12; a is a number having a value from 1 to 6.
38. The composition of Claim 37 wherein in formula II, R₁ is a monovalent organic radical having from 8 to 16 carbon atoms, b is zero, and a is a number having a value of from 1 to 2.
 39. The composition of Claim 1 further including a photoinitiator.
 40. The composition of Claim 39 wherein the photoinitiator is at least one member selected from the group consisting of benzildimethyl ketal, 2,2-diethoxy-1,2-diphenylethanone, 1-hydroxy-cyclohexyl-phenyl ketone, α,α -dimethoxy- α -hydroxy acetophenone, 1-(4-isopropylphenyl)-2-hydroxy-2-methyl-propan-1-one, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-propan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, 3,6-bis(2-methyl-2-morpholino-propanonyl)-9-butyl-carbazole, 4,4'-bis(dimethylamino)benzophenone, 2-chlorothioxanthone, 4-chlorothioxanthone, 2-isopropylthioxanthone, 4-isopropylthioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 4-benzoyl-N,N-dimethyl-N-[2-(1-oxo-2-propenyl)oxy]ethylbenzenemethanaminium chloride, methyl-diethanolamine, triethanolamine, ethyl 4-(dimethylamino)benzoate, 2-n-butoxyethyl 4-(dimethylamino)benzoate and combinations thereof.
 41. The composition of Claim 1 further including a colorant.
 42. The composition of Claim 41 wherein the colorant is a blue pigment and the composition further includes a 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone and thioxanthone.
 43. The composition of Claim 1 wherein the urethane oligomer is at least one member selected from the group consisting of aliphatic urethane acrylate oligomer and aromatic urethane acrylate oligomer.
 44. A photopolymerized resin obtained by the energy polymerization of the composition of any one of Claims 1 to 43.
 45. A screen coated with a coating material comprising the composition as defined in any one of claims 1 to 43.
 46. The screen of claim 45 wherein said screen is fabricated from a material selected from the group consisting of silk, polyester, polypropylene, high density polyethylene, nylon glass, nickel, aluminum and steel.
 47. The screen of Claim 45 wherein said coating material is cured.
 48. The screen of Claim 47 wherein the screen is engraved with indicia.
 49. In a method for coating a substrate in which an energy-curable polymer-forming composition is applied by applicator means to a substrate and the polymer forming composition is thereafter exposed to a source of energy under such conditions as to form a coating of cured polymer on the substrate, an improvement comprising
 - a) employing the applicator means for applying the substantially water-free, water-washable, energy-curable, polymer-forming composition as defined in any one of claims 1 to 43, and
 - b) washing the applicator means with water to remove excess polymer-forming composition therefrom.
 50. The method of Claim 49 wherein the step of employing the applicator means for applying the polymer-forming composition comprises a method selected from the group consisting of dipping, brushing, spraying and rolling.
 51. The method of Claim 49 wherein the substrate is a porous screen which, with the coating of cured polymer provides a blank stencil.
 52. The method of Claim 51 further including the step of engraving the blank stencil to form a printing mask.
 53. The method of Claim 51 wherein said engraving step is performed by means of a laser.
 54. The method of Claim 49 wherein the source of energy includes electron beam radiation or UV radiation.
 55. The method of Claim 54 wherein the source of UV radiation provides a UV radiation energy density of from 2000 to 3000 mJ/cm².
 56. The method of Claim 49 wherein the substrate is metal or a textile.

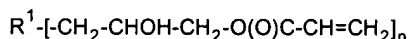
Patentansprüche

1. Im Wesentlichen wasserfreie, mit Wasser waschbare, durch Energie härtbare, polymerbildende Zusammensetzung, umfassend:

- a) ein Oligomer, das aus der aus Epoxy-Oligomer und Urethan-Oligomer bestehenden Gruppe ausgewählt ist, wobei das Oligomer wenigstens zwei ethylenisch ungesättigte Reste aufweist;
 b) wenigstens ein alkoxyliertes Polyol-Monomer, das wenigstens zwei ethylenisch ungesättigte Reste aufweist und zur Copolymerisation mit der Oligomer-Komponente (a) befähigt ist, um ein festes gehärtetes Polymer bereitzustellen, wenn es Polymerisationsbedingungen unter Einwirkung von Energie ausgesetzt wird, und
 c) ein Zucker-Tensid, das aus der aus einem Polyhydroxy-Fettsäureamid, einem Alkylpolyglycosid und Mischungen derselben bestehenden Gruppe ausgewählt ist.

2. Zusammensetzung gemäß Anspruch 1, wobei das Epoxy-Oligomer ein Epoxyacrylat-Oligomer ist.

3. Zusammensetzung gemäß Anspruch 2, wobei das Epoxyacrylat-Oligomer sich von einer Verbindung der Formel



ableitet, in der R^1 ein aliphatischer Rest, ein aromatischer Rest oder ein Arenrest ist, der wenigstens zwei Kohlenstoffatome und wenigstens zwei Oxidoreste aufweist, und n eine ganze Zahl von 2 bis 6 ist.

4. Zusammensetzung gemäß Anspruch 3, wobei R^1 ein Bisphenol-Rest ist.

5. Zusammensetzung gemäß Anspruch 3, wobei R^1 aus der aus einem Hydrochinon-Rest und einem Catechin-Rest bestehenden Gruppe ausgewählt ist.

6. Zusammensetzung gemäß Anspruch 3, wobei R^1 eine geradkettige oder verzweigt-kettige Alkylgruppe mit 2 bis 6 Kohlenstoffatomen einschließt.

7. Zusammensetzung gemäß Anspruch 6, wobei R^1 aus der Gruppe ausgewählt ist, bestehend aus einem Ethylenglycol-Rest, Propylenglycol-Rest, Trimethylolpropan-Rest, Pentaerythrit-Rest, Neopentylglycol-Rest, Glyceryl-Rest, Diglyceryl-Rest, Inositol-Rest und Sorbit-Rest.

8. Zusammensetzung gemäß Anspruch 3, wobei R^1 ein gesättigter oder ungesättigter, geradkettiger oder verzweigt-kettiger Rest mit 6 bis 24 Kohlenstoffatomen ist.

9. Zusammensetzung gemäß Anspruch 8, wobei R^1 ein epoxidierter Sojaöl-Rest ist.

10. Zusammensetzung gemäß Anspruch 3, wobei R^1 ein Polyethylenglycol-Rest ist.

11. Zusammensetzung gemäß Anspruch 3, wobei R^1 ein Ethylenoxid-Propylenoxid-Copolymer ist.

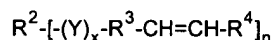
12. Zusammensetzung gemäß Anspruch 1, wobei das Epoxy-Oligomer thixotropisch ist.

13. Zusammensetzung gemäß Anspruch 1, wobei das Epoxy-Oligomer durch Umsetzung eines Diepoxids mit einer Säure-Komponente, die eine ethylenisch ungesättigte Carbonsäure oder ein reaktives Derivat derselben aufweist, in Gegenwart eines Polyamids, das sich von einer polymerisierten Fettsäure ableitet, erhalten wird.

14. Zusammensetzung gemäß Anspruch 13, wobei die Säure-Komponente Acrylsäure ist.

15. Zusammensetzung gemäß Anspruch 13, wobei das Diepoxid ein Diglycidylether eines zweiwertigen Phenols ist.

16. Zusammensetzung gemäß Anspruch 1, wobei das alkoxylierte Polyol-Monomer die Formel

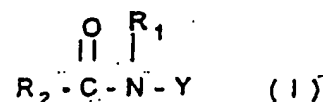


hat, in der R^2 ein aliphatischer Rest, ein aromatischer Rest oder ein Arenrest ist, der wenigstens zwei Kohlenstoffatome und wenigstens zwei Oxidoreste aufweist, Y ein Alkylenoxid-Rest ist und x eine ganze Zahl von 2 bis 6 ist, R^3 eine Bindungsgruppe ist, die den Alkylenoxid-Rest Y mit der $-CH=CH$ -Gruppe verbinden kann, R^4 Wasserstoff oder $-C(O)OR^5$ ist, wobei R^5 Wasserstoff oder eine Alkylgruppe mit 1 bis 22 Kohlenstoffatomen ist, und n eine ganze Zahl von 2 bis 6 ist.

17. Zusammensetzung gemäß Anspruch 16, wobei R^2 ein Bisphenol-Rest oder eine Gruppe ist, die aus der aus einem Hydrochinon-Rest und einem Catechin-Rest bestehenden Gruppe ausgewählt ist.

18. Zusammensetzung gemäß Anspruch 16, wobei R^2 eine geradkettige oder verzweigt-kettige Alkylgruppe mit 2 bis 6 Kohlenstoffatomen einschließt.

19. Zusammensetzung gemäß Anspruch 16, wobei R² aus der Gruppe ausgewählt ist, bestehend aus einem Ethylenglycol-Rest, Propylenglycol-Rest, Trimethylolpropan-Rest, Pentaerythrit-Rest, Neopentylglycol-Rest, Glyceryl-Rest, Diglyceryl-Rest, Inositol-Rest und Sorbit-Rest. 5
20. Zusammensetzung gemäß Anspruch 16, wobei R² ein gesättigter oder ungesättigter, geradkettiger oder verzweigt-kettiger Rest mit 6 bis 24 Kohlenstoffatomen ist. 10
21. Zusammensetzung gemäß Anspruch 16, wobei R² ein epoxidiertes Sojaöl-Rest, ein Polyethylenglycol-Rest oder ein Ethylenoxid-Propylenoxid-Copolymer ist. 15
22. Zusammensetzung gemäß Anspruch 16, wobei Y ein Ethylenoxid-Rest ist. 20
23. Zusammensetzung gemäß Anspruch 16, wobei R³ ein Rest ist, der aus der Gruppe ausgewählt ist, bestehend aus -O-, -O(O)CO-, -OCH₂CH₂- und -OCH₂CHOHCH₂O(O)C-. 25
24. Zusammensetzung gemäß Anspruch 16, wobei das wenigstens eine alkoxylierte Polyol-Monomer eine Mischung aus wenigstens einem alkoxylierten Polyoldiacrylat und wenigstens einem alkoxylierten Polyoltriacylat umfasst. 30
25. Zusammensetzung gemäß Anspruch 24, wobei die Zusammensetzung einen Kontaktwinkel auf Nickel von nicht mehr als 100° aufweist. 35
26. Zusammensetzung gemäß Anspruch 24, wobei die Zusammensetzung 5 % bis 30 % des wenigstens einen alkoxylierten Polyoldiacrylats und 5 % bis 30 % des wenigstens einen alkoxylierten Polyoltriacylats, bezogen auf das Gesamtgewicht der Zusammensetzung, einschließt. 40
27. Zusammensetzung gemäß Anspruch 2, wobei die Zusammensetzung 10 % bis 25 % des wenigstens einen alkoxylierten Polyoldiacrylats und 10 % bis 25 % des wenigstens einen alkoxylierten Polyoltriacylats, bezogen auf das Gesamtgewicht der Zusammensetzung, einschließt. 45
28. Zusammensetzung gemäß Anspruch 24, wobei die Zusammensetzung 15 % bis 20 % des wenigstens einen alkoxylierten Polyoldiacrylats und 15 % bis 20 % des wenigstens einen alkoxylierten Polyoltriacylats, bezogen auf das Gesamtgewicht der Zusammensetzung, einschließt. 50
29. Zusammensetzung gemäß Anspruch 24, wobei das wenigstens eine alkoxylierte Polyoltriacylat Trimethylolpropanethoxylattriacylat ist, und das wenigstens eine alkoxylierte Polyoldiacrylat eine Verbindung ist, die aus der Gruppe ausgewählt ist, bestehend aus Bisphenol-A-ethoxylatdiacylat, Neopentylglycolpropoxylatdiacylat und deren Mischungen. 55
30. Zusammensetzung gemäß Anspruch 29, wobei das Epoxy-Oligomer sich von Bisphenol-A-epoxydiacylat ableitet.
31. Zusammensetzung gemäß Anspruch 29, wobei die Monomer-Mischung 10 - 15 Gew.-% Neopentylglycolpropoxylatdiacylat und 15 - 20 Gew.-% Trimethylolpropanethoxylattriacylat, bezogen auf das Gesamtgewicht der Zusammensetzung, einschließt.
32. Zusammensetzung gemäß Anspruch 31, wobei die Monomer-Mischung weiterhin 5 - 10 % Bisphenol-A-ethoxylatdiacylat einschließt.
33. Zusammensetzung gemäß Anspruch 31, wobei das Epoxy-Oligomer durch Umsetzung eines Diepoxids mit einer Säure-Komponente, die eine ethylenisch ungesättigte Carbonsäure oder ein reaktives Derivat derselben aufweist, in Gegenwart eines Polyamids, das sich von einer polymerisierten Fettsäure ableitet, erhalten wird.
34. Zusammensetzung gemäß Anspruch 33, wobei die Säure-Komponente Acrylsäure ist.
35. Zusammensetzung gemäß Anspruch 33, wobei das Diepoxid ein Diglycidylether eines zweiwertigen Phenols ist.
36. Zusammensetzung gemäß Anspruch 1, wobei das Zucker-Tensid ein Polyhydroxy-Fettsäureamid ist, das der Formel I



entspricht, in der R₁ H, ein C₁-C₄-Kohlenwasserstoffrest, ein 2-Hydroxyethyl-Rest, ein 2-Hydroxypropyl-Rest oder eine Mischung derselben ist, und R₂ ein C₅-C₃₁-Kohlenwasserstoffrest ist, Y ein Polyhydroxy-Kohlenwasserstoffrest mit einer linearen Kohlenwasserstoffkette ist, in der wenigstens 3 Hydroxylgruppen direkt an die Kette gebunden sind, oder ein alkoxyliertes Derivat (vorzugsweise ethoxyliert oder propoxyliert) desselben ist.

37. Zusammensetzung gemäß Anspruch 1, wobei das Zucker-Tensid ein Alkylpolyglycosid ist, das der Formel II



entspricht, in der R_1 ein einbindiger organischer Rest mit 6 bis 30 Kohlenstoffatomen ist, R_2 ein zwei-bindiger Alkylen-Rest mit 2 bis 4 Kohlenstoffatomen ist, Z ein Saccharid-Rest mit 5 oder 6 Kohlenstoffatomen ist, b eine Zahl mit einem Wert von 0 bis 12 ist, a eine Zahl mit einem Wert von 1 bis 6 ist.

38. Zusammensetzung gemäß Anspruch 37, wobei in der Formel II R_1 ein einbindiger organischer Rest mit 8 bis 16 Kohlenstoffatomen ist, b Null ist und a eine Zahl eines Wertes von 1 bis 2 ist.
39. Zusammensetzung gemäß Anspruch 1, die weiterhin einen Photoinitiator einschließt.
40. Zusammensetzung gemäß Anspruch 39, wobei der Photoinitiator wenigstens eine Verbindung ist, die aus der Gruppe ausgewählt ist, bestehend aus Benzildimethylketal, 2,2-Diethoxy-1,2-diphenylethanon, 1-Hydroxycyclohexylphenylketon, α,α -Dimethoxy- α -hydroxyacetophenon, 1-(4-Isopropylphenyl)-2-hydroxy-2-methylpropan-1-on, 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methylpropan-1-on, 2-Methyl-1-[4-(methylthio)-phenyl]-2-morpholinopropan-1-on, 2-Benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-butan-1-on, 3,6-Bis(2-methyl-2-morpholinopropanonyl)-9-butylcarbazol, 4,4'-Bis(dimethylamino)benzophenon, 2-Chlorthioxanthon, 4-Chlorthioxanthon, 2-Isopropylthioxanthon, 4-Isopropylthioxanthon, 2,4-Dimethylthioxanthon, 2,4-Diethylthioxanthon, 4-Benzoyl-N,N-dimethyl-N-[2-(1-oxo-2-propenyl)oxy]ethylbenzolmethanaminiumchlorid, Methyl-diethanolamin, Triethanolamin, Ethyl-4-(dimethylamino)benzoat, 2-n-Butoxyethyl-4-(dimethylamino)benzoat und Kombinationen derselben.
41. Zusammensetzung gemäß Anspruch 1, die weiterhin ein Färbemittel einschließt.
42. Zusammensetzung gemäß Anspruch 41, wobei das Färbemittel ein blaues Pigment ist, und die Zusammensetzung weiterhin 2-Benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanon und Thioxanthon einschließt.
43. Zusammensetzung gemäß Anspruch 1, wobei das Urethan-Oligomer wenigstens eine Verbindung ist, die aus der Gruppe ausgewählt ist, bestehend aus einem aliphatischen Urethanacrylat-Oligomer und

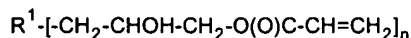
einem aromatischen Urethanacrylat-Oligomer.

44. Photopolymerisiertes Harz, das durch Polymerisation der Zusammensetzung gemäß irgendeinem der Ansprüche 1 bis 43 unter Einwirkung von Energie erhalten wird.
45. Raster, das mit einem Beschichtungsmaterial beschichtet ist, das die Zusammensetzung gemäß irgendeinem der Ansprüche 1 bis 43 umfasst.
46. Raster gemäß Anspruch 45, wobei das Raster aus einem Material hergestellt wird, das aus der Gruppe ausgewählt ist, bestehend aus Seide, Polyester, Polypropylen, Polyethylen hoher Dichte, Nylon, Glas, Nickel, Aluminium und Stahl.
47. Raster gemäß Anspruch 45, in dem das Beschichtungsmaterial gehärtet ist.
48. Raster gemäß Anspruch 47, wobei das Raster mit Buchstaben oder Abbildungen (indicia) graviert ist.
49. Verfahren zum Beschichten eines Substrats, wobei eine durch Energie härtbare, polymerbildende Zusammensetzung durch eine Auftragsvorrichtung auf ein Substrat aufgetragen wird, und die polymerbildende Zusammensetzung danach einer Energiequelle unter derartigen Bedingungen ausgesetzt wird, dass eine Beschichtung von gehärtetem Polymer auf dem Substrat gebildet wird, **dadurch gekennzeichnet, dass**
- a) die Auftragsvorrichtung verwendet wird, um die im Wesentlichen wasserfreie, mit Wasser waschbare, durch Energie härtbare, polymerbildende Zusammensetzung gemäß irgendeinem der Ansprüche 1 bis 43 aufzutragen, und
- b) die Auftragsvorrichtung mit Wasser gewaschen wird, um überschüssige, polymerbildende Zusammensetzung davon zu entfernen.
50. Verfahren gemäß Anspruch 49, wobei der Schritt der Verwendung der Auftragsvorrichtung, um die polymerbildende Zusammensetzung aufzutragen, ein Verfahren umfasst, das aus der aus Eintauchen, Aufstreichen, Sprühen und Walzen bestehenden Gruppe ausgewählt ist.
51. Verfahren gemäß Anspruch 49, in welchem das Substrat ein poröses Raster ist, wobei die Beschichtung von gehärtetem Polymer eine Blankoschablone bereitstellt.
52. Verfahren gemäß Anspruch 51, das weiterhin den Schritt des Gravierens der Blankoschablone unter Bildung einer Druckmaske einschließt.

53. Verfahren gemäß Anspruch 51, wobei der Schritt des Gravierens durch einen Laser durchgeführt wird.
54. Verfahren gemäß Anspruch 49, wobei die Energiequelle Elektronenstrahl-Strahlung oder UV-Strahlung einschließt.
55. Verfahren gemäß Anspruch 54, wobei die UV-Strahlungsquelle eine UV-Strahlungsenergiedichte von 2000 bis 3000 mJ/cm³ bereitstellt.
56. Verfahren gemäß Anspruch 49, wobei das Substrat ein Metall oder Textilerzeugnis ist.

Revendications

1. Composition formant polymère substantiellement exempte d'eau, lavable à l'eau, et réticulable sous énergie, qui comprend :
- a) un oligomère choisi dans le groupe constitué par un oligomère époxy et un oligomère uréthane, ledit oligomère ayant au moins deux groupements éthyléniquement insaturés ;
- b) au moins un monomère polyol alcoxylé qui a au moins deux groupements éthyléniquement insaturés et qui est capable d'être copolymérisé avec un composant oligomère (a) pour fournir un polymère solide réticulé quand il est exposé à des conditions de polymérisation par énergie ; et,
- c) un surfactant à base de sucre choisi dans le groupe constitué par un amide d'un acide gras polyhydroxyle, un polyglycoside alkyle, et les mélanges de ceux-ci.
2. Composition selon la revendication 1 dans laquelle l'oligomère époxy est un oligomère époxy-acrylate.
3. Composition selon la revendication 2 dans laquelle l'oligomère époxy-acrylate est dérivé d'un composé de formule :

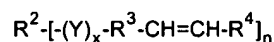


dans laquelle R¹ est un groupement aliphatique, aromatique ou arène ayant au moins deux atomes de carbone et au moins deux résidus oxydo, et n est un entier valant de 2 à 6.

4. Composition selon la revendication 3 dans laquelle R¹ est un résidu bisphénol.
5. Composition selon la revendication 3 dans laquelle R¹ est choisi dans le groupe constitué par un résidu

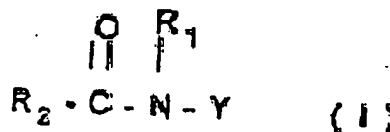
hydroquinone et un résidu catéchol.

6. Composition selon la revendication 3 dans laquelle R¹ comprend un groupe alkyle à chaîne linéaire ou ramifiée de 2 à 6 atomes de carbone.
7. Composition selon la revendication 6 dans laquelle R¹ est choisi dans le groupe constitué par les résidus éthylène glycol, propylène glycol, triméthylolpropane, pentaérythritol, néopentyle glycol, glycéryle, diglycéryle, inositol, et sorbitol.
8. Composition selon la revendication 3 dans laquelle R¹ est un groupement aliphatique, saturé ou insaturé, à chaîne linéaire ou ramifiée de 6 à 24 atomes de carbone.
9. Composition selon la revendication 8 dans laquelle R¹ est un résidu d'huile de soja époxydée.
10. Composition selon la revendication 3 dans laquelle R¹ est un groupement polyéthylène glycol.
11. Composition selon la revendication 3 dans laquelle R¹ est un copolymère d'oxyde éthylène et d'oxyde de propylène.
12. Composition selon la revendication 1 dans laquelle l'oligomère époxy est thixotropique.
13. Composition selon la revendication 1 dans laquelle l'oligomère époxy est obtenu par réaction d'un diépoxyde avec un composant acide qui possède un acide carboxylique éthyléniquement insaturé ou un dérivé réactif de celui-ci en présence d'un polyamide dérivé d'un acide gras polymérisé.
14. Composition selon la revendication 13 dans laquelle le composant acide est l'acide acrylique.
15. Composition selon la revendication 14 dans laquelle le diépoxyde est l'éther diglycidyle d'un dihydroxybenzène.
16. Composition selon la revendication 1 dans laquelle le monomère polyol alcoxylé de formule :



dans laquelle R² est un groupement aliphatique, aromatique ou arène ayant au moins deux atomes de carbone et au moins deux résidus oxydo, Y est un groupement oxyde d'alkylène et x est un entier valant de 2 à 6, R³ est un groupe de liaison capable de joindre le groupement oxyde d'alkylène Y et le groupe -CH=CH-, R⁴ est hydrogène ou -C(O)OR⁵ dans lequel R⁵ est hydrogène ou un groupe alkyle

- ayant de 1 à 22 atomes de carbone, et n est un entier valant de 2 à 6.
17. Composition selon la revendication 16 dans laquelle R² est un résidu bisphénol ou un groupe choisi dans le groupe constitué par un résidu hydroquinone et un résidu catéchol. 5
 18. Composition selon la revendication 16 dans laquelle R² comprend un groupe alkyle à chaîne linéaire ou ramifiée de 2 à 6 atomes de carbone. 10
 19. Composition selon la revendication 16 dans laquelle R² est choisi dans le groupe constitué par les résidus éthylène glycol, propylène glycol, triméthylolpropane, pentaérythritol, néopentyle glycol, glycéryle, diglycérile, inositol, et sorbitol. 15
 20. Composition selon la revendication 16 dans laquelle R² est un groupement aliphatique, saturé ou insaturé, à chaîne linéaire ou ramifiée de 6 à 24 atomes de carbone. 20
 21. Composition selon la revendication 16 dans laquelle R² est un résidu d'huile de soja époxydée, un groupement polyéthylène glycol ou un copolymère d'oxyde d'éthylène et d'oxyde de propylène. 25
 22. Composition selon la revendication 16 dans laquelle Y est un résidu oxyde d'éthylène. 30
 23. Composition selon la revendication 16 dans laquelle R³ est un élément choisi dans le groupe constitué par -O-, -O(O)C-, -OCH₂CH₂- et -OCH₂CHOHCH₂O(O)C-. 35
 24. Composition selon la revendication 16 dans laquelle le au moins un monomère polyol alcoxylé comprend un mélange d'au moins un polyol alcoxylé diacrylate et d'au moins un polyol alcoxylé triacrylate. 40
 25. Composition selon la revendication 24 dans laquelle la composition présente un angle de contact sur le nickel qui n'est pas supérieur à 100 °. 45
 26. Composition selon la revendication 24 dans laquelle la composition comprend 5 % à 30 % du au moins un monomère polyol alcoxylé diacrylate et 5 % à 30 % du au moins un monomère polyol alcoxylé triacrylate, calculé sur le poids total de la composition. 50
 27. Composition selon la revendication 2 dans laquelle la composition comprend 10 % à 25 % du au moins un monomère polyol alcoxylé diacrylate et 10 % à 25 % en poids du au moins un monomère polyol alcoxylé triacrylate, calculé sur le poids total de la composition. 55
 28. Composition selon la revendication 24 dans laquelle la composition comprend 15 % à 20 % du au moins un monomère polyol alcoxylé diacrylate, et 15 % à 20 % du au moins un monomère polyol alcoxylé triacrylate calculé, sur le poids total de la composition.
 29. Composition selon la revendication 24 dans laquelle le au moins un polyol alcoxylé triacrylate est l'éthoxylate de triméthylolpropane triacrylate et le au moins un polyol alcoxylé diacrylate est un élément choisi dans le groupe constitué par l'éthoxylate de bisphénol A diacrylate, le propoxylate de néopentyle glycol diacrylate et les mélanges de ceux-ci.
 30. Composition selon la revendication 29 dans laquelle l'oligomère époxy est dérivé de l'époxy-acrylate de bisphénol A.
 31. Composition selon la revendication 29 dans laquelle le mélange de monomères comprend 10 % à 15 % en poids de propoxylate de néopentyle glycol diacrylate, et de 15 % à 20 % en poids d'éthoxylate de triméthylolpropane triacrylate, calculé sur le poids total la composition.
 32. Composition selon la revendication 31 dans laquelle le mélange de monomères comprend en outre 5 % à 10 % d'éthoxylate de bisphénol A diacrylate.
 33. Composition selon la revendication 31 dans laquelle l'oligomère époxy est obtenu par réaction d'un diépoxyde avec un composant acide qui possède un acide carboxylique éthyléniquement insaturé ou un dérivé réactif de celui-ci en présence d'un polyamide dérivé d'un acide gras polymérisé.
 34. Composition selon la revendication 33 dans laquelle le composant acide est l'acide acrylique.
 35. Composition selon la revendication 33 dans laquelle le diépoxyde est l'éther diglycidyle d'un dihydroxybenzène.
 36. Composition selon la revendication 1 dans laquelle le surfactant à base de sucre est un amide d'un acide gras polyhydroxyle correspondant à la formule I :



dans laquelle R¹ est hydrogène, hydrocarbyle en

- C₁-C₄, 2-hydroxy éthyle, 2-hydroxy propyle, ou un mélange de ceux-ci ; et R² est un groupement hydrocarbyle en C₅-C₃₁ ; et Y est un groupement polyhydroxyhydrocarbyl possédant une chaîne hydrocarbyle linéaire avec au moins trois hydroxyles directement liés à la chaîne, ou un dérivé alcoxylé (de préférence éthoxylé ou propoxylé) de celui-ci.
37. Composition selon la revendication 1 dans laquelle le surfactant à base de sucre est un polyglycoside alkyle correspondant à la formule II :
- $$R_1O(R_2O)_b(Z)_a \quad (II)$$
- dans laquelle R₁, est un radical organique monovalent ayant de 6 à 30 atomes de carbone ; R₂ est un radical alkylène divalent ayant de 2 à 4 atomes de carbone ; Z est un résidu saccharide ayant de 5 à 6 atomes de carbone ; b est un nombre ayant une valeur de 0 à 12 ; a est un nombre ayant une valeur de 1 à 6.
38. Composition selon la revendication 37 dans laquelle dans la formule II, R₁ est un radical organique monovalent ayant de 8 à 16 atomes de carbone, b vaut zéro, et a est un nombre ayant une valeur de 1 à 2.
39. Composition selon la revendication 1 comprenant en outre un photoinitiateur.
40. Composition selon la revendication 39 dans laquelle le photoinitiateur est au moins un élément choisi dans le groupe constitué par le benzylidiméthyl kétal, la 2,2-diéthoxy-1,2-diphényléthanone, la 1-hydroxy-cyclohexyl-phényl cétone, l'α,α-diméthoxy-α-hydroxy acétophénone, la 1-(4-isopropyl-phényl)-2-hydroxy-2-méthyl-propan-1-one la 1-[4-(2-hydroxyéthoxy)phényl]-2-hydroxy-2-méthyl-propan-1-one, la 2-méthyl-1-[4-(méthylthio)phényl]-2-morpholino-propan-1-one, la 2-benzyl-2-N,N-diméthylamino-1-(4-morpholinophényl)-butan-1-one, la 3,6-bis(2-méthyl-2-morpholino-propanonyl)-9-butyl-carbazole, la 4,4'-bis(diméthylamino)-benzophénone, la 2-chlorothioxanthone, la 4-chlorothioxanthone, la 2-isopropylthioxanthone, la 4-isopropylthioxanthone, la 2,4-diméthylthioxanthone, la 2,4-diéthylthioxanthone, le chlorure de 4-benzoyl-N,N-diméthyl-N-[2-(1-oxo-2-propényl)oxy]éthylbenzène-méthanaminium, la méthyl-diéthanolamine, la triéthanolamine, le benzoate d'éthyl-4-(diméthylamino), le benzoate de 2-n-butoxyéthyl-4-(diméthylamino) et les combinaisons de ceux-ci.
41. Composition selon la revendication 1 comprenant en outre un colorant.
42. Composition selon la revendication 41 dans laquelle le colorant est un pigment bleu et la composition comprend en outre une 2-benzyl-2-N,N-diméthylamino-1-(4-morpholinophényl)-1-butanone et une thioxanthone.
43. Composition selon la revendication 1 dans laquelle l'oligomère uréthane est au moins un élément choisi dans le groupe constitué par un oligomère acrylate uréthane aliphatique et un oligomère acrylate uréthane aromatique.
44. Résine photopolymérisée obtenue par polymérisation sous énergie de la composition de l'une quelconque des revendications 1 à 43.
45. Ecran revêtu d'un matériau de revêtement comprenant la composition selon l'une quelconque des revendications 1 à 43.
46. Ecran selon la revendication 45 dans laquelle ledit écran est fabriqué à partir d'un matériau choisi dans le groupe constitué par la soie, le polyester, le polypropylène, le polyéthylène haute densité, le nylon, le verre, le nickel, l'aluminium et l'acier.
47. Ecran selon la revendication 45 dans lequel ledit matériau est réticulé.
48. Ecran selon la revendication 47 dans lequel l'écran est gravé avec une empreinte.
49. Dans un procédé pour revêtir un substrat, selon lequel une composition formant polymère, réticulable sous énergie est appliquée par moyen applicateur sur un substrat et la composition formant polymère est ensuite exposée à une source d'énergie sous des conditions qui permettent de former un revêtement de polymère réticulé sur le substrat, l'amélioration comprenant :
- l'utilisation du moyen applicateur pour l'application de la composition formant polymère, substantiellement exempte d'eau, lavable à l'eau, et réticulable sous énergie selon l'une quelconque des revendications 1 à 43.
 - le lavage de l'applicateur avec de l'eau pour éliminer de celui-ci l'excès de composition pour la mise en forme de polymère.
50. Procédé selon la revendication 49, dans lequel l'étape d'utilisation du moyen applicateur pour appliquer la composition formant polymère comprend un procédé choisi dans le groupe constitué par le trempage, le brossage, la pulvérisation et le roulage.
51. Procédé selon la revendication 49 dans lequel le

substrat est un écran poreux qui, avec le revêtement de polymère réticulé fournit un stencil vierge.

52. Procédé selon la revendication 51 comprenant en outre l'étape de gravure du stencil vierge pour former un masque d'impression. 5
53. Procédé selon la revendication 51 dans lequel ladite étape de gravure est effectuée au moyen d'un laser. 10
54. Procédé selon la revendication 49 dans lequel la source d'énergie comprend le rayonnement de faisceau d'électrons ou le rayonnement ultraviolet. 15
55. Procédé selon la revendication 54 dans lequel la source de rayonnement ultraviolet fournit une densité d'énergie de rayonnement ultraviolet de 2000 à 3000 mJ/cm². 20
56. Procédé selon la revendication 49 dans lequel le substrat est du métal ou un textile. 25

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